UNIVERSITY OF PENNSYLVANIA

THE FREE ENERGY OF DILUTION OF SULPHURIC ACID IN THE PRESENCE OF CERTAIN SULPHATE ELECTROLYTES

R. D. STURGIS

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA
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Introduction

The activity coefficient of one electrolyte in the presence of another may be determined by measurements of the solubility or by electromotive forces of suitable cells. The first method although applicable to many electrolytes in many salt solutions cannot be applied to solutions of substances such as hydrochloric acid, sulphuric acid, etc. The activity coefficient of hydrochloric acid in solutions of uniunivalent chlorides,[1] and biunivalent chlorides[2] has been obtained by measurement of the electromotive forces of the concentration cell without liquid junction of the type

$$\begin{array}{l} Ag \mid AgCl \mid HCl \quad (C_1) \mid H_2 \mid HCl \quad (C_1) \mid AgCl \mid Ag \\ \qquad\qquad\quad \mid MeCl_x(C) \quad \mid \end{array}$$

where $MeCl_x$ represents an alkali or alkaline earth chloride. The net effect of this cell is the transfer of a mol of acid from the acid-salt mixture to the pure acid, and from its electromotive force, the free energy of transfer of the acid may be obtained and subsequently its activity and activity coefficient.

Since no measurements of this kind are available on the free energy of transfer of an electrolyte of a higher valence type from salt solution to the pure electrolyte, the present investigation was undertaken. Measurements of cells of the types

$$H_2 \mid H_2SO_4(C_1) \qquad \overset{I}{Me}_2SO_4(C) \mid Hg_2SO_4 \mid Hg$$

and

$$H_2 \mid H_2SO_4(C_1) \qquad \overset{II}{Me}SO_4(C) \mid Hg_2SO_4 \mid Hg$$

where $\overset{I}{Me}$ represents sodium or potassium and $\overset{II}{Me}$ represents

[1] Loomis, Essex and Meacham, *Jour. Amer. Chem. Soc.*, 39, 1133 (1917); Ming Chow, *ibid.*, 42, 497 (1920); Harned, *ibid.*, 45, 1808 (1920).

[2] Harned and Brumbaugh, *ibid.*, 44, 2729 (1922).

magnesium have been made. From these by subtraction of the electromotive force of the cell containing the salt from that of the pure acid, the electromotive forces of the concentration cells with liquid junctions

$$Hg \mid Hg_2SO_4 \mid H_2SO_4(C_1) \quad M\overset{I}{e}_2SO_4(C) \mid H_2 \mid H_2SO_4(C) \mid Hg_2SO_4 \mid Hg$$

and

$$Hg \mid Hg_2SO_4 \mid H_2SO_4(C_1) \quad M\overset{II}{e}SO_4(C) \mid H_2 \mid H_2SO_4(C) \mid Hg_2SO_4 \mid Hg$$

are obtained, respectively. The electromotive forces of these latter cells correspond to free energy of transfer of sulphuric acid from the salt solution to the pure acid solution. From these measurements the relative partial free energies and activity coefficients of the acid at 0.01 and 0.1 molal concentrations in salt solutions of different strengths may be computed. Further, results have also been obtained for varying strengths of acid and salt at constant total molality.

The free energy of dilution of sulphuric acid in aqueous solution has been carefully measured by several investigators who employed the cell

$$Hg \mid Hg_2SO_4 \mid \underset{(C_1)}{H_2SO_4} \mid H_2 \mid \underset{(C_2)}{H_2SO_4} \mid Hg_2SO_4 \mid Hg.$$

Brönsted[3] investigated this cell over rather a wide concentration range. Lewis and Lacy[4] made measurements using 0.005 and 0.05 molal acid. More recent work has been done by Randall and Cushman.[5] These studies along with freezing point measurements have been employed by Lewis and Randall[6] for computing the activity coefficients of sulphuric acid. Moreover, the precautions necessary for obtaining reproducible cell measurements are carefully described in the above contributions and in this study the procedure recommended therein has been followed.

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[3] *Zeit. physik. Chem.*, 68, 693 (1910).
[4] *Jour. Amer. Chem. Soc.*, 36, 804 (1914).
[5] *Jour. Amer. Chem. Soc.*, 40, 393 (1918).
[6] "Thermodynamics," p. 355; McGraw-Hill Book Company, 1923.

Preparation of Materials

All water used for the preparation of solutions was redistilled from an alkaline permanganate solution through a block tin condenser. Four times distilled mercury was employed. Mercurous sulphate was prepared electrolytically from a portion of this mercury by the method of Hulett.[1] It was almost white in color and electrodes prepared from samples of this material which were made at different times showed no variation in potential greater than ± 0.05 of a millivolt.

Sodium and potassium sulphates were recrystallized from ordinary distilled water. The crystals were centrifuged and the process of recrystallization was repeated until solutions of the salt gave no test for the chloride ion. After this treatment the two salts were recrystallized twice from the redistilled water. In the purification of the sodium salt advantage was taken of the decreased solubility of the anhydrous salt above 33° C.

Approximately 100-gram portions were ignited to dull redness and held at that temperature for ten minutes or longer. While still hot the crucible was placed in a vacuum desicator over sulphuric acid. Saturated solutions of the salt in conductivity water were carefully examined for neutrality. In all cases their reaction to litmus was neutral.

Magnesium sulphate was recrystallized twice using doubly distilled water. A nearly saturated solution was then made and carefully analyzed. All solutions of this salt were prepared by weighing portions of this solution. This standard solution was neutral toward litmus.

The solution of sulphuric acid was prepared by diluting the pure acid to a concentration of approximately 4 molal. This solution was analyzed by precipitation of barium sulphate. The analyses showed a maximum variation of less than 0.05 per cent of the total sulphuric acid content. Portions of the stock solution were weighed out and diluted to the desired strength.

Hydrogen was prepared by the electrolysis of a solution of

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[1] *Phys. Rev.*, 32, 257 (1911).

sodium hydroxide. It was then passed through an alkaline pyrogallol solution and soda-lime before entering the cell apparatus.

Description of Apparatus

The cell was of the H type and consisted of two limbs of about 50 c.c. capacity each, which were separated by an arm 10 cm. long, 8 mm. diameter. A glass stop-cock on the arm served to separate the two electrode compartments and to prevent any mercurous sulphate from being carried mechanically into the hydrogen electrode compartment. Pure hydrogen entered the cell through a glass tube sealed into the bottom of the hydrogen electrode compartment. This gas was saturated with the vapor of the solution in the cell by bubbling through a saturator which consisted of a U-shaped tube containing the cell solution. One arm of this tube contained bulbs at regular intervals and was at such an angle that very efficient saturation of the vapor was rapidly attained. That this was the case was proved by the fact that the cells could be run continuously for forty-eight hours without a change in potential due to evaporation.

A short platinum wire was sealed through the bottom of the other limb of the cell and a mercury contact was made by means of a glass tube sealed to the cell around this wire. A thin piece of platinum foil welded to a short platinum wire and fused into a suitable glass tube was used as the electrode. The glass tube when filled with mercury was supported in the hydrogen compartment of the cell by means of a rubber stopper. Another hole in the stopper permitted the exit of the hydrogen. This was fitted with a small bubbler, which served to prevent air from entering the cell.

The electrode was platinized by making it the cathode in a chlorplatinic acid solution, using a current density strong enough to liberate gas freely at the cathode. The deposit was black, adherent, smooth, and velvety, and gave uniformly reproducible results.

Four standard cadmium cells were prepared according to the

method of Hulett[2]; using cadmium purified by two fractional distillations in hydrogen.

The cadmium sulphate was twice crystallized from conductivity water. The preparation of the mercury and mercurous sulphate used in the cells has already been described. Each cell was checked separately against a standard Weston cell. The electromotive forces of these cells differed from the mean value by ± 0.01 of a millivolt. The four were connected in parallel and mounted on a board in a thermostat. Their electromotive forces were compared with the cell employed as standard each week.

The Type R, Leeds and Northrup galvanometer was found to be sufficiently sensitive for this investigation. An Otto Wolff 15,000 ohm potentiometer was employed.

The thermostat was filled with water and electrically heated and stirred. By means of a fine capillary at the top of the mercury regulator controlling the heating element, the temperature was easily maintained at 25 degrees $\pm 0.01°$.

Procedure

The cell was carefully cleaned, washed with distilled water, and then a dry dust-free current of air was passed through until dried. A layer of purest dry mercury sufficient to cover the sealed-in platinum wire was next introduced into the mercury-mercurous sulphate electrode compartment, and finally, a portion of mercurous sulphate washed at least six times by thorough shaking and decantation with the solution to be used in the cell, was cautiously added in order not to displace the mercury at the bottom and thus wet the wire. It was observed by Randall and Cushman[3] that reproducible results could not be obtained if the platinum lead in wire were wetted with the solution in the cell. During this operation the stop-cock between the two limbs was kept closed to prevent particles of mercurous sulphate from flowing into the limb bearing the platinum electrode.

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[2] *Phys. Rev.*, 32, 257 (1911).

[3] *Jour. Amer. Chem. Soc.*, 40, 393 (1918).

The other limb was next filled with the solution and the platinum electrode inserted after four washings with the cell solution. After assembling the apparatus and saturator, the cell was immersed in the bath to a point slightly above the level of the solution in the cell.

During the first part of this investigation the platinum electrode was completely immersed and so placed near the bottom of the limb that the bubbles of hydrogen impinged upon its lower edge. Later on, however, the electrode was only half immersed in the solution and equilibrium seemed to be attained more rapidly by the latter arrangement. In nearly every experiment a slow current of hydrogen (about ten bubbles a minute) was bubbled through the cell all night before readings were taken and then the electromotive force of the cell was measured after it had remained constant over a period of from six to eight hours.

The electromotive force of the cell was first balanced against the electromotive force of two large unsaturated cadmium sulphate cells in series, of the design described by Hulett.[4] Immediately after making a cell measurement the Hulett cells were balanced against the four standardized cadmium cells. The desired electromotive force was computed from the ratio of the potentiometer readings. The mean value of five constant readings was taken as the electromotive force. The barometer was read at the beginning and end, and once or twice during the measurements of a cell. A correction for the actual hydrogen pressure ($P_b - P_{H_2O}$), where P_b is barometric pressure and P_{H_2O} is the vapor pressure of water at 25° C. was made according to the thermodynamic formula

$$E = \frac{RT}{2F} \ln \frac{760}{P_{H_2}}$$

where P_{H_2} is the hydrogen pressure. Thus, all electromotive forces are referred to hydrogen at one atmosphere pressure.

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[4] *Loc. cit.*

Experimental Results

In Table I are given the electromotive forces of the cells

$$H_2 \mid H_2SO_4(0.1) \quad (Me_xSO_4(C)) \mid Hg_2SO_4 \mid Hg$$

at 25° C. The concentration of all the electrolytes is expressed in mols (formula weight) in 1000 grams of water. Column 1 contains the salt concentration; column 2 the electromotive forces at the hydrogen pressures given in column 3. Column 4 contains the correction for the hydrogen pressure, and column 5 the electromotive forces of the cells at 1 atmosphere pressure.

Table I.—Electromotive Forces of the Cells

$H_2 \mid H_2SO_4(0.1)$ $(Me_xSO_4(C)) \mid Hg_2SO_4 \mid Hg$

(1)	(2)	(3)	(4)	(5)
(C)	(E)	(P_H)	Correction	E (corr.)
0.00	0.73697	744.2	0.00027	0.73724
0.00	0.73673	731.3	0.00047	0.73720
....	.....	.....	.....	0.73722 mean
		Potassium Sulphate		
0.10	0.73983	760.8	0.00038	0.74021
0.20	0.74388	729.2	0.00051	0.74439
0.30	0.74728	735.8	0.00040	0.74768
0.50	0.75290	729.2	0.00051	0.75341
		Sodium Sulphate		
0.10	0.73908	744.2	0.00025	0.73933
0.20	0.74236	750.9	0.00015	0.74251
0.30	0.74450	726.8	0.00055	0.74505
0.50	0.74790	727.7	0.00050	0.74840
1.00	0.75195	734.8	0.00042	0.75237

Magnesium Sulphate

0.10	0.73801	731.1	0.00048	0.73849
0.10	0.73793	733.5	0.00044	0.73837
....	.....	.....	.....	0.73843 mean
0.20	0.73931	724.3	0.00060	0.73991
0.30	0.74050	735.6	0.00040	0.74090
0.50	0.74171	739.5	0.00034	0.74205
1.00	0.74136	725.5	0.00057	0.74193
1.00	0.74156	733.9	0.00043	0.74199
....	.....	.....	.....	0.74196 mean

In Table II are given the similar series of results of the electromotive forces of the cells

$$H_2 \mid H_2SO_4(0.01) \quad (Me_xSO_4(C)) \mid Hg_2SO_4 \mid Hg$$

at 25° C. The column headings have the same significance as in Table I.

TABLE II.—ELECTROMOTIVE FORCES OF THE CELLS

$H_2 \mid H_2SO_4(0.01 \quad Me_xSO_4(C)) \mid Hg_2SO_4 \mid Hg$

(1)	(2)	(3)	(4)	(5)
(C)	(E)	(P_H)	CORRECTION	E (corr.)
0.00	0.79660	739.2	0.00034	0.79694
0.00	0.79678	740.1	0.00033	0.79711
0.00	0.79670	734.0	0.00043	0.79713
....	.....	.....	.....	0.79706 mean

Potassium Sulphate

0.02	0.79508	747.0	0.00021	0.79529
0.03	0.79556	746.8	0.00022	0.79578
0.05	0.79654	729.8	0.00050	0.79704
0.09	0.79958	733.9	0.00043	0.80001
0.10	0.80027	745.9	0.00023	0.80050
0.20	0.80525	743.8	0.00026	0.80551
0.30	0.80816	725.2	0.00058	0.80874
0.50	0.81371	723.9	0.00060	0.81431
0.50	0.81410	733.3	0.00044	0.81454
....	.....	.....	.....	0.81443 mean

Sodium Sulphate

0.02	0.79455	732.3	0.00046	0.79501
0.05	0.79594	739.0	0.00034	0.79628
0.09	0.79853	732.1	0.00046	0.79899
0.10	0.79918	742.5	0.00029	0.79947
0.20	0.80332	747.3	0.00021	0.80353
0.30	0.80588	741.0	0.00031	0.80619
0.50	0.80872	744.7	0.00025	0.80897
1.00	0.81370	739.5	0.00034	0.81404

Magnesium Sulphate

0.02	0.79475	729.5	0.00051	0.79526
0.05	0.79554	726.6	0.00056	0.79610
0.10	0.79716	736.1	0.00039	0.79755
0.20	0.79954	745.0	0.00025	0.79979
0.30	0.80100	745.0	0.00025	0.80125
0.50	0.80223	746.0	0.00023	0.80246
1.00	0.80138	732.7	0.00045	0.80183

Table III contains the results of the cells at constant total molality. C_1 in column is the molal acid strength, and $(C + C_1)$ equals 0.1.

TABLE III.—ELECTROMOTIVE FORCES OF THE CELLS

$H_2 \mid H_2SO_4(C_1) \quad Me_xSO_4(C)) \mid Hg_2SO_4 \mid Hg$

0.10 Molal Total Concentration

(1)	(2)	(3)	(4)	(5)
(C_1)	(E)	(P_H)	CORRECTION	E (CORR.)
		Potassium Sulphate		
0.003	0.83070	733.4	0.00044	0.83114
0.010	0.79958	733.9	0.00043	0.80001
0.020	0.78106	743.0	0.00028	0.78134
0.030	0.76978	728.1	0.00053	0.77031
0.050	0.75550	730.2	0.00050	0.75600
0.070	0.74630	740.1	0.00032	0.74662
0.100	*	*	*	0.73722

* NOTE: See Table I.

Sodium Sulphate

0.003	0.82962	735.4	0.00041	0.83003
0.010	0.79853	732.1	0.00046	0.79899
0.020	0.78001	743.0	0.00028	0.78029
0.030	0.76926	739.2	0.00034	0.76960
0.050	0.7550	730.2	0.00050	0.75550
0.070	0.74585	740.1	0.00032	0.74617

CALCULATION OF ACTIVITY COEFFICIENTS

Both the values of the electromotive force of this cell containing 0.01 and 0.1 molal acid concentration fall on the curve of the results of Randall and Cushman.[5] The result at 0.01

[5] *Jour. Amer. Chem. Soc.*, 40, 393 (1918).

molal acid concentration is about 7 millivolts lower than that obtained by Brönsted.[6] Although concordance is obtained, the activity coefficient ratio between the 0.1 and 0.01 molal solutions does not agree with the results obtained by other methods. This point has been fully discussed by Lewis and Randall.[7] They attribute the discrepancy to the solubility of mercurous sulphate at these low acid concentrations. Indeed, at concentrations below 0.01 molal, indications of the formation of the yellow basic sulphate of mercury are observable. This, as well as the solubility, may produce the discrepancy. In calculating the activity coefficients from the above electromotive forces, 0.313 has been taken as the activity coefficient of the acid at 0.1 molal concentration.[8] All other values have been computed from this one.

As previously shown, if the value of the electromotive force of the cell containing salt be subtracted from that containing the acid, the electromotive force ΔE of the concentration cell with liquid junction is obtained. ΔE is related to the activity product of the ions of the acid by the thermodynamic equation

$$\Delta E = \frac{3\,RT}{2\,F} \ln \frac{\sqrt[3]{a^2_{H(s)}\, a_{SO_4(s)}}}{\sqrt[3]{a^2_H\, a_{SO_4}}} = \frac{3\,RT}{2\,F} \ln \frac{a_{\pm(s)}}{a_\pm} \qquad (1)$$

where the subscript (s) refers to the solution, and where $a_\pm$ represents the cube root of the activity product of the acid. The activity coefficient of the acid may be computed by the equation

$$\gamma = \frac{a_\pm}{(C^2_H\, C_{SO_4})^{1/3}} \qquad (2)$$

where γ is the activity coefficient and C_H and C_{SO_4} are the stoichiometrical molal concentrations of the hydrogen and sulphate ions.

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[6] *Zeit. physik. Chem.*, 68, 693 (1920).

[7] "Thermodynamics," p. 356; McGraw-Hill Book Company (1923).

[8] Lewis and Randall, "Thermodynamics," p. 354; McGraw-Hill Book Company (1923).

From the results in Tables I and II, and by means of equations (1) and (2) the values of the activity coefficients of the acid in the sulphate solutions have been computed. These are compiled in Table IV. Column 1 contains the molal salt concentration; column 2 the ionic strength of the solution, and column 3 contains the activity coefficient of the acid.

TABLE IV.—THE ACTIVITY COEFFICIENT OF SULPHURIC ACID IN SULPHATE SOLUTIONS

0.10 M. Sulphuric Acid			*0.01 M. Sulphuric Acid*		
(1)	(2)	(3)	(1)	(2)	(3)
(C)	μ	γ	(C)	μ	γ
Potassium Sulphate					
0.00	0.30	0.313	0.00	0.03	0.662
0.10	0.60	0.230	0.02	0.09	0.481
0.20	0.90	0.180	0.03	0.12	0.431
0.30	1.20	0.150	0.05	0.18	0.365
0.50	1.80	0.113	0.09	0.30	0.285
....	....	.....	0.10	0.33	0.272
....	....	.....	0.20	0.63	0.193
....	....	.....	0.30	0.93	0.156
....	....	.....	0.50	1.53	0.114
Sodium Sulphate					
0.10	0.60	0.235	0.02	0.09	0.484
0.20	0.90	0.190	0.05	0.18	0.372
0.30	1.20	0.161	0.09	0.30	0.292
0.50	1.80	0.129	0.10	0.33	0.280
1.00	3.30	0.095	0.20	0.63	0.203
....	....	.....	0.30	0.93	0.166
....	....	.....	0.50	1.53	0.131
....	....	.....	1.00	3.03	0.092

Magnesium Sulphate

0.10	0.70	0.241	0.02	0.11	0.481
0.20	1.10	0.202	0.05	0.23	0.374
0.30	1.50	0.179	0.10	0.43	0.294
0.50	2.30	0.152	0.20	0.83	0.224
1.00	4.30	0.124	0.30	1.23	0.189
....	....	.....	0.50	2.03	0.155
....	....	.....	1.00	4.03	0.126

The activity coefficients of the 0.1 and 0.01 molal acid in the salt solutions given in this table are plotted against the ionic strength in Figures 1 and 2, respectively. The values of γ for the pure acid taken from Lewis and Randall's calculation are also given.

The Activity Coefficient of Sulphuric Acid in Sodium and Potassium Sulphate Solutions at 0.1 Total Molality

From the electromotive force data in Table III, and by means of equations (1) and (2), it is possible to compute the activity coefficient of the acid in potassium and sodium sulphate at 0.1 total molal concentration. The results of such a calculation are given in Table V. The columns contain the molal acid concentration, the activity coefficient of the acid and its logarithm, respectively.

Electromotive force measurements of a similar nature have been made. Loomis, Essex and Meacham[9] found a slight decrease in the activity coefficient in hydrochloric acid and salt mixtures in going from 0.1 to 0.01 m. acid. Ming Chow[10] who extended the series from 0.01 to 0.0001, concluded from his results that the activity coefficient remained constant throughout that range. However, his results fell off slightly between 0.1 and 0.01 molal acid concentration. This was also observed by Harned and Brumbaugh.[11] It is a point of considerable interest

[9] *Loc. cit.*
[10] *Loc. cit.*
[11] *Loc. cit.*

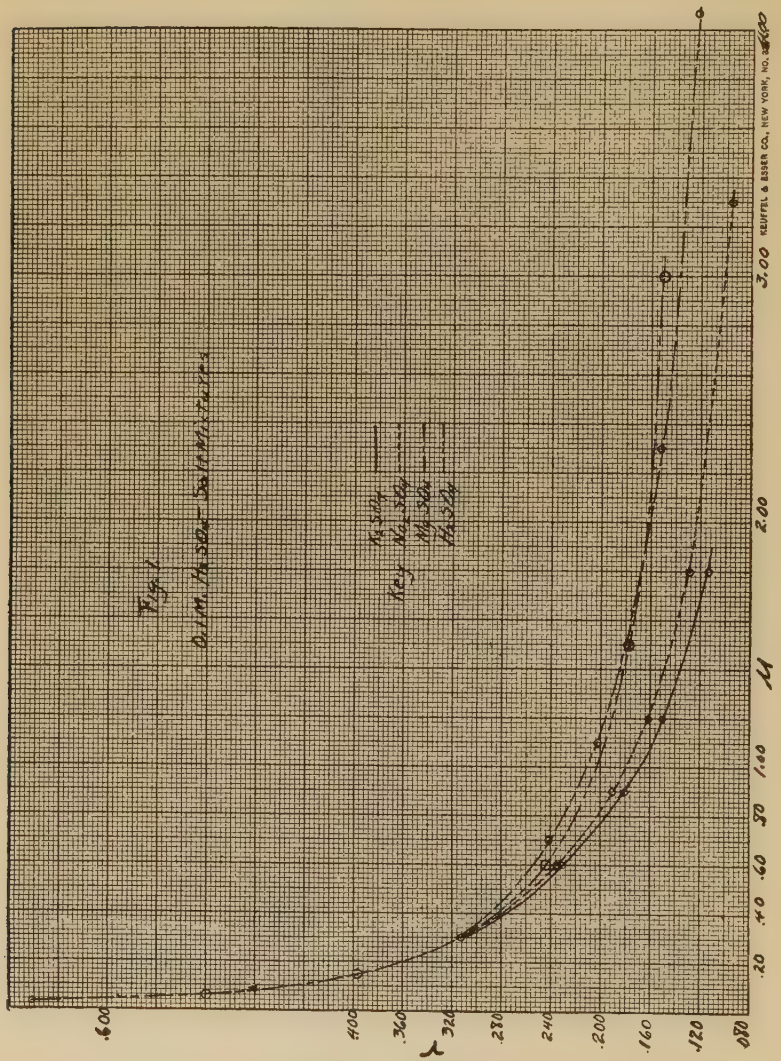


Fig. 1
Dilution of H_2SO_4 Solutions
Key
H_2SO_4
Na_2SO_4
$MgSO_4$
$ZnSO_4$
λ
μ_1
.600
.400
.360
.320
.280
.240
.200
.160
.120
.080
.20
.40
.60
.80
1.00
2.00
3.00
KEUFFEL & ESSER CO., NEW YORK, NO.

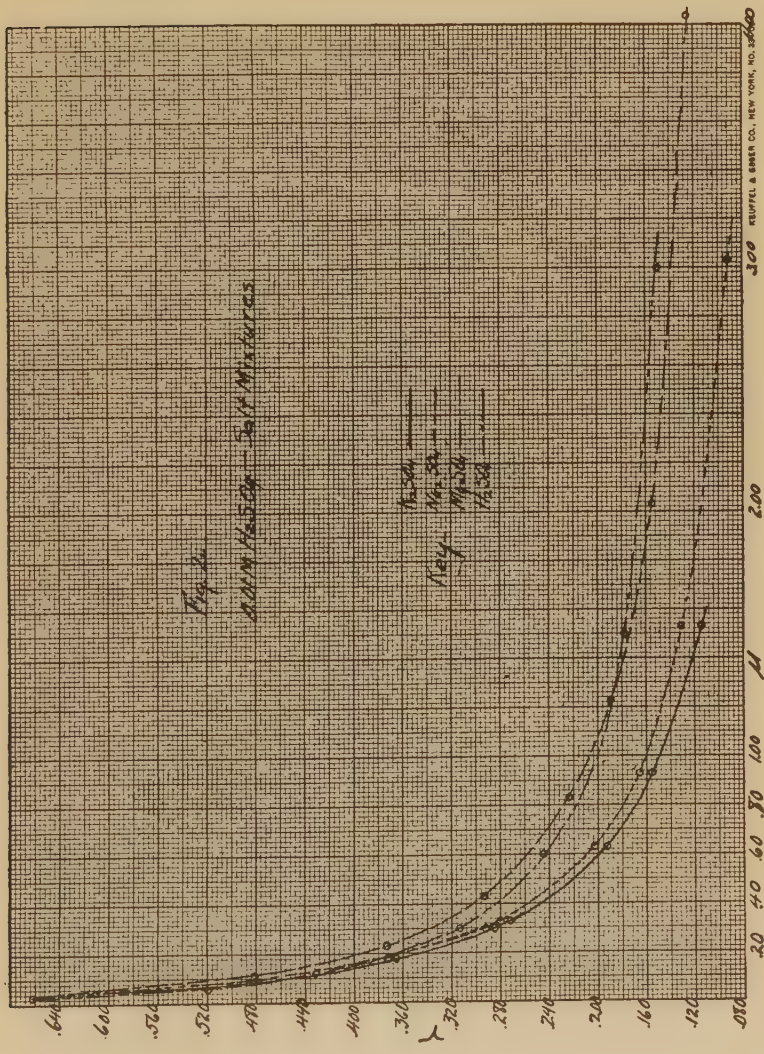


Fig. 1.
Mn(NH4)2(SO4)2 — Salt Mixtures
Key: N=.24 N=.32 N=.36
μ
γ
.20 .40 .60 .80 1.00 2.00 3.00
.040 .080 .120 .160 .200 .240 .280 .320 .360 .400 .440 .480 .520 .560 .600 .640
KEUFFEL & ESSER CO., NEW YORK, NO. 336

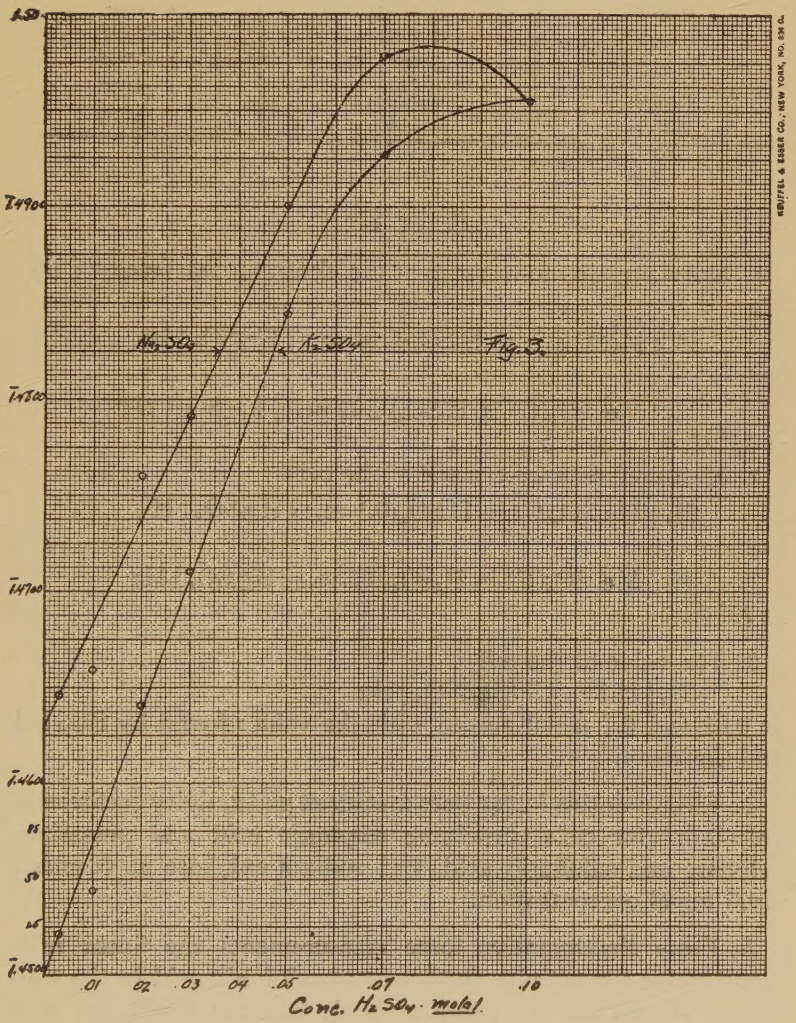
to find out whether the logarithm of the activity coefficient varies linearly with the concentration of the acid at total molal concentration. That this is true for hydrochloric acid in potassium chloride mixtures in the region of 0.01 to 0.1 was shown by Harned and Brumbaugh.[12] Brönsted[13] has also obtained much evidence for such a linear variation for other electrolytes in other solvents from solubility data in solutions under 0.1 molal total concentration. In Figure 3 are plotted the values of the logarithm of the activity coefficient for sulphuric acid in the presence of potassium sulphate and sodium sulphate against the concentration of sulphuric acid. From the present careful measurements the linear relation does not hold in the region between 0.07 and 0.1 molal but appears to hold with considerable exactness in the region of 0.003 to 0.06 molal sulphuric acid concentration. Although this does not prove that an exact linear relationship exists, it is excellent evidence that the activity coefficient of the acid does not remain constant in a solution of this total ionic strength.

TABLE V.—ACTIVITY COEFFICIENT OF SULPHURIC ACID IN SULPHATE SOLUTIONS AT 0.1 MOLAL TOTAL CONCENTRATION

(1)	(2)	(3)
(C_1)	(γ)	LOG. γ
	Potassium Sulphate	
0.003	0.2832	$\bar{1}$.45213
0.010	0.2847	$\bar{1}$.45439
0.020	0.2911	$\bar{1}$.46413
0.030	0.2958	$\bar{1}$.47105
0.050	0.3051	$\bar{1}$.48444
0.070	0.3110	$\bar{1}$.49274
0.100	0.313	$\bar{1}$.49554

[12] *Loc. cit.*

[13] *Jour. Amer. Chem. Soc.*, 44, 877 (1922); *ibid.*, 45, 2898 (1923).


1.490
1.480
1.470
1.460
1.450
.01
.02
.03
.04
.05
.07
.10
Conc. H_2SO_4 · molal.
H_2SO_4
K_2SO_4
Fig. 3.

Sodium Sulphate

0.003	0.2915	$\bar{1}.46463$
0.010	0.2923	$\bar{1}.46589$
0.020	0.2992	$\bar{1}.47597$
0.030	0.3013	-1.47906
0.050	0.3090	1.49007
0.070	0.3146	1.49780

Summary

1. Measurements were made of the electromotive forces of the cells

$$H_2 \mid M\dot{e}SO_4(C) \text{ in } H_2SO_4(0.01 \text{ m.}) \mid Hg_2SO_4 \mid Hg$$

and

$$H_2 \mid M\ddot{e}\ SO_4(C) \text{ in } H_2SO_4(0.01 \text{ m.}) \mid Hg_2SO_4 \mid Hg$$

at 25° C.

2. Measurements were made of the cells

$$H_2 \mid M\dot{e}\ SO_4(C) \text{ in } H_2SO_4(0.1 \text{ m.}) \mid Hg_2SO_4 \mid Hg$$

and

$$H_2 \mid M\ddot{e}\ SO_4(C) \text{ in } H_2SO_4(0.1 \text{ m.}) \mid Hg_2SO_4 \mid Hg$$

at 25° C.

3. The value of the cell

$$H_2 \mid H_2SO_4(C) \mid Hg_2SO_4 \mid Hg$$

at 0.01 and 0.1 molal agreed with the values found by Randall and Cushman.

4. Electromotive forces were measured and activity coefficients calculated for cells containing sulphuric acid and potassium sulphate and sulphuric acid, and sodium sulphate at constant total molal concentration.

5. From electromotive force measurements the linear relationship for the activity coefficient of sulphuric acid in the constant 0.10 molal salt solutions holds between 0.003 and 0.06 molal acid concentration.

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